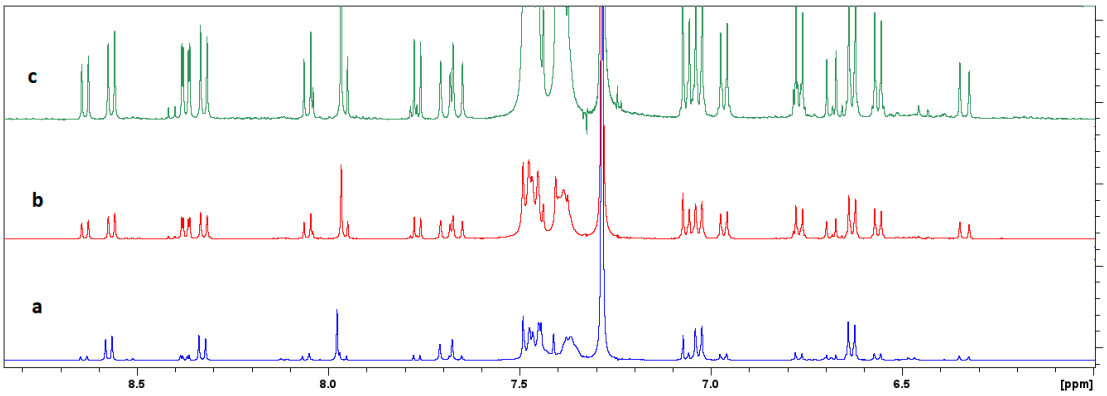

Figure S1: ^{1}H-NMR spectra (aromatic region) of 1 in $CDCl_3$ solutions (500 MHz, 298K): (a) an "aged" sample, (b) irradiated at λ=365 nm for 10 min, (c) irradiated for an additional 30 min.

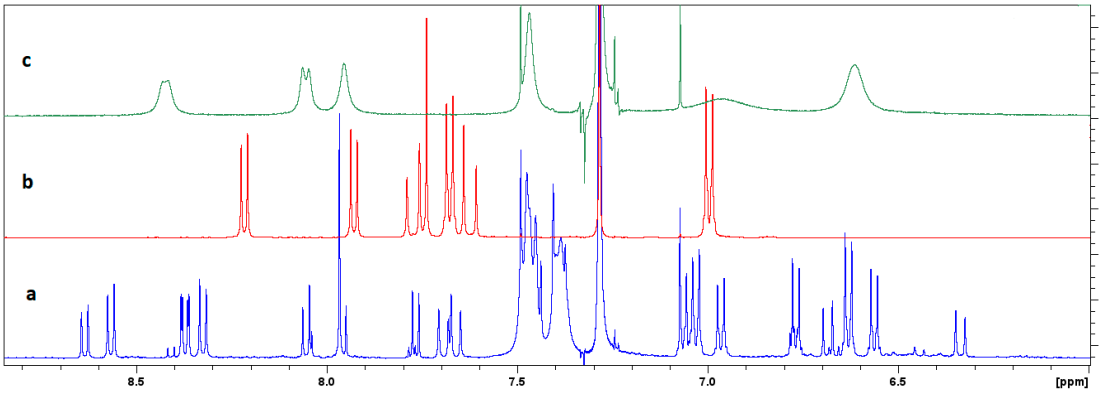

Figure S2: ^{1}H-NMR spectra (aromatic region) of $CDCl_3$ solutions of: (a) 1 irradiated at λ=365 nm for 40 min, (b) L, (c) $[AgL_2]^+$.

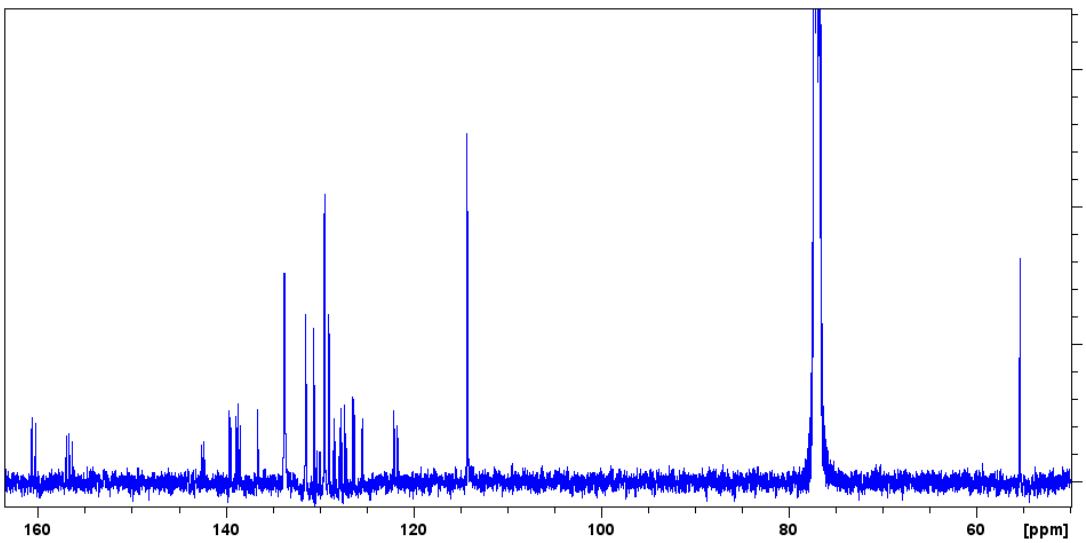

Figure S3: $^{13}C\{^{1}H\}$-NMR spectrum of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min (125 MHz, 298K).

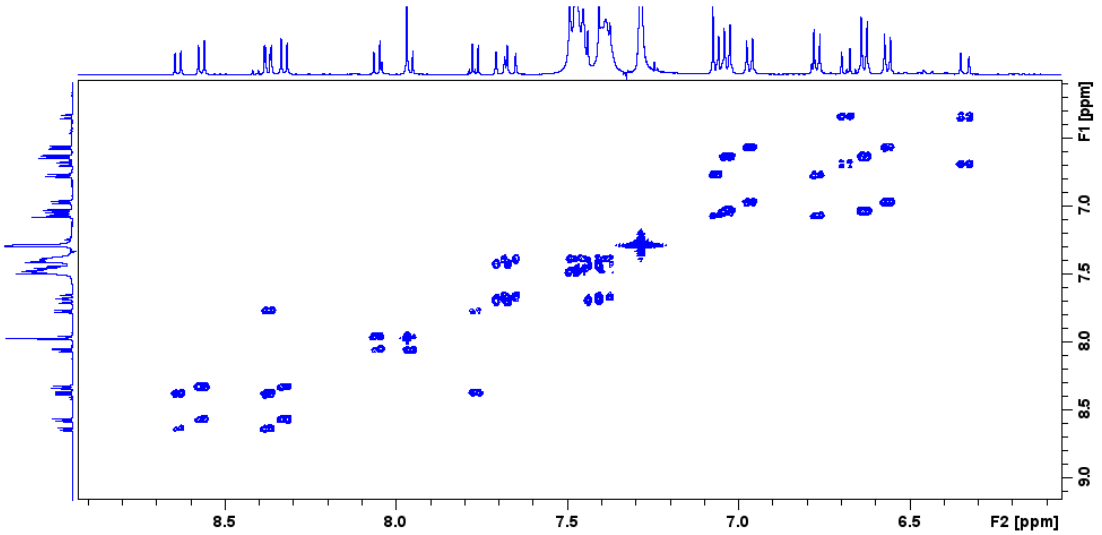

Figure S4: ^{1}H-^{1}H-COSY NMR spectrum (500 MHz, 298K) of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min.

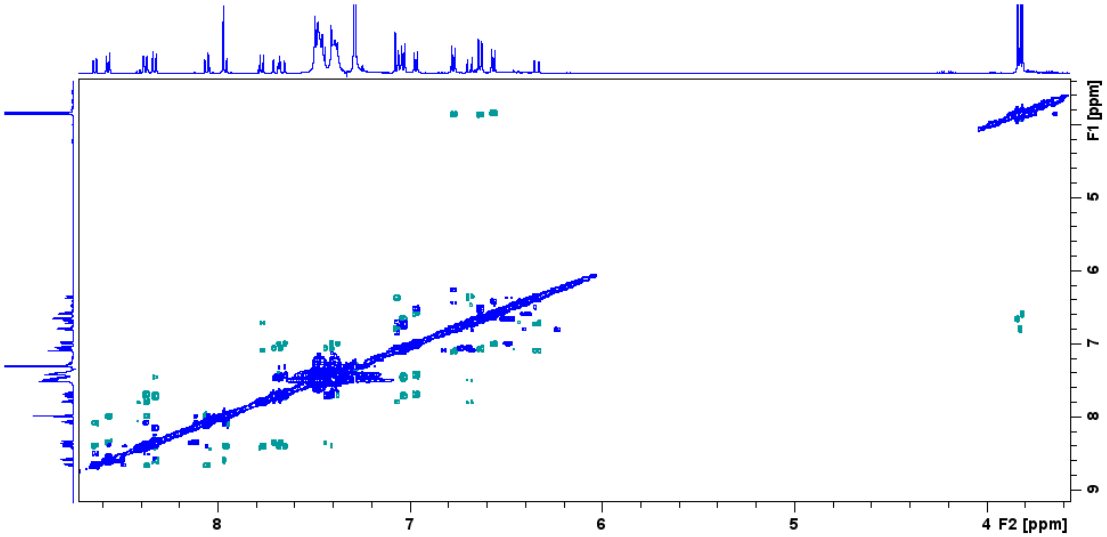

Figure S5: ^{1}H-^{1}H-NOESY NMR spectrum (500 MHz, 298K) of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min.

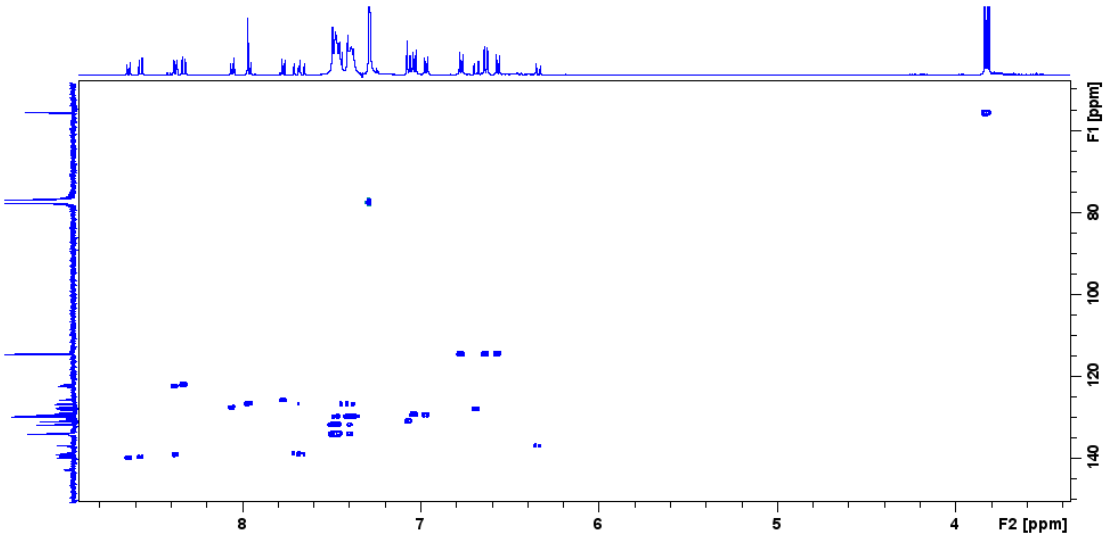

Figure S6: ^{1}H-^{13}C-HSQC NMR spectrum (298K) of a CDCl3 solution of 1 irradiated at λ=365 nm for 40 min.

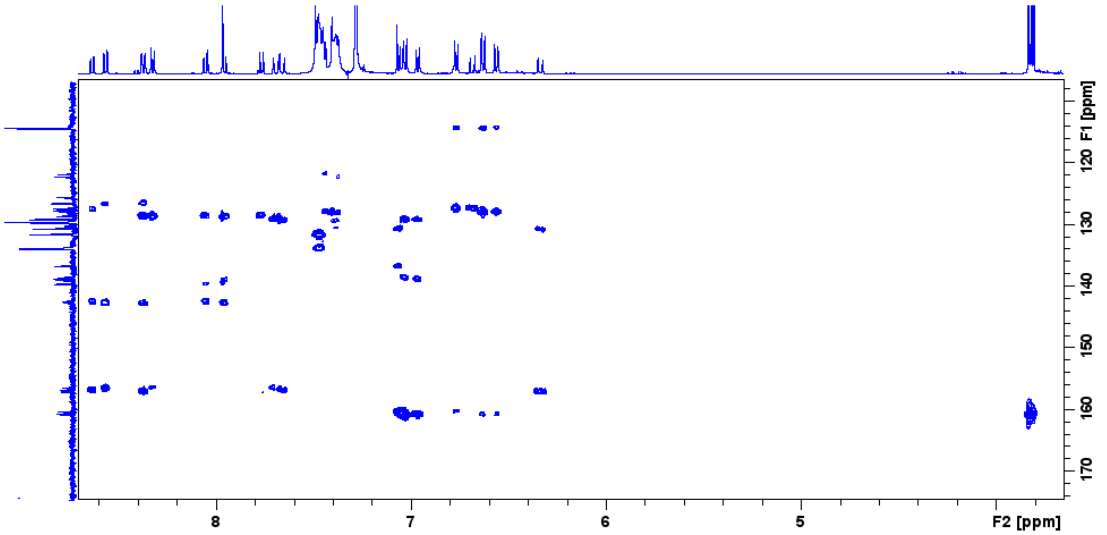

Figure S7: ^{1}H-^{13}C-HMBC NMR spectrum (500 MHz, 298K) of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min.

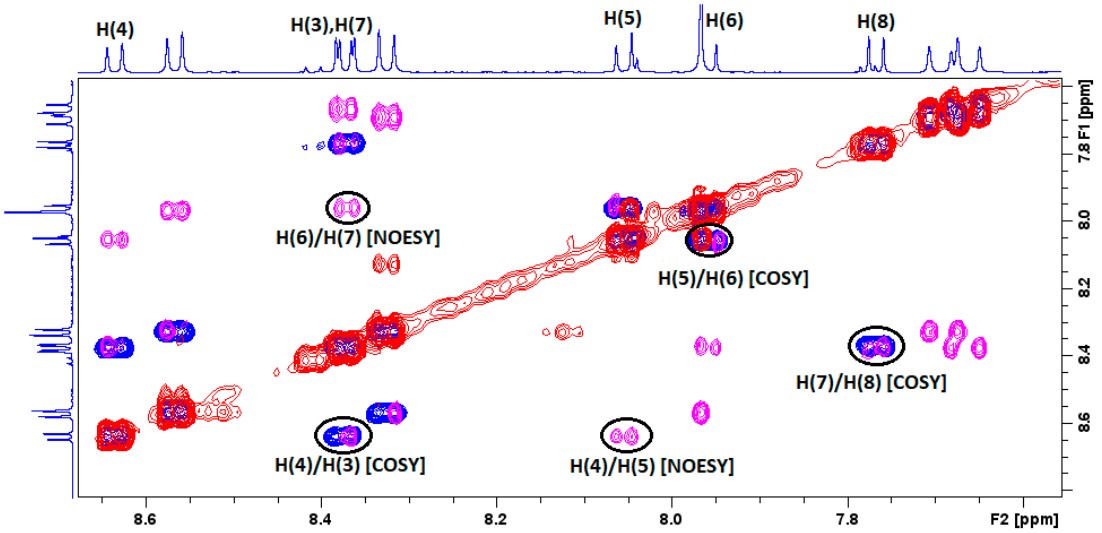

Figure S8: Overlay of ^{1}H-^{1}H-COSY (blue) and ^{1}H-^{1}H-NOESY (red-magenta) NMR spectra of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min. The most informative correlations toward identification of the phen core ^{1}H's are circled.

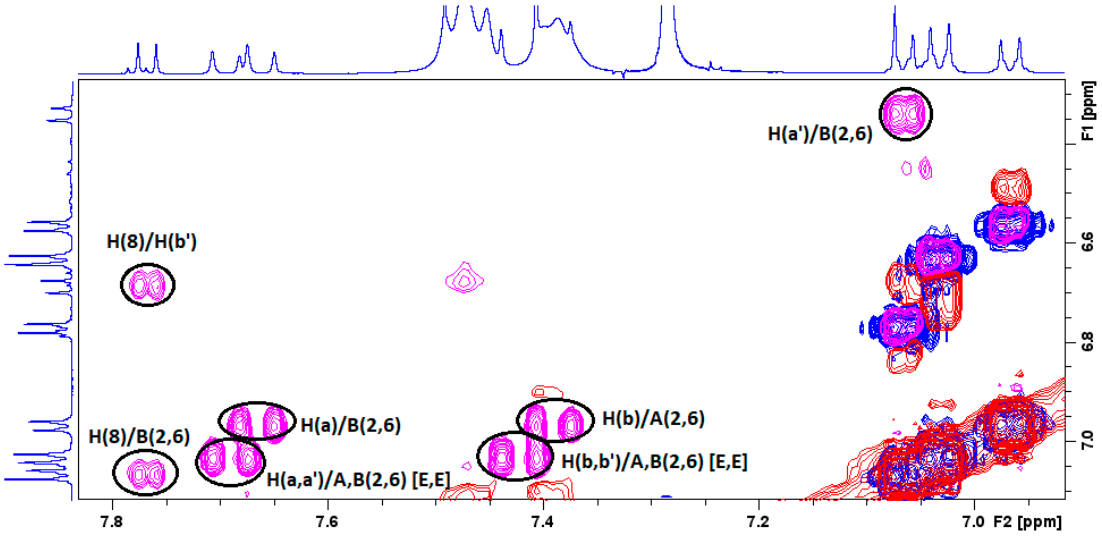

Figure S9: Overlay of ^{1}H-^{1}H-COSY (blue) and ^{1}H-^{1}H-NOESY (red-magenta) NMR spectra of a $CDCl_3$ solution of 1 irradiated at λ=365 nm for 40 min, showing the NOE correlations from ethylenic protons.

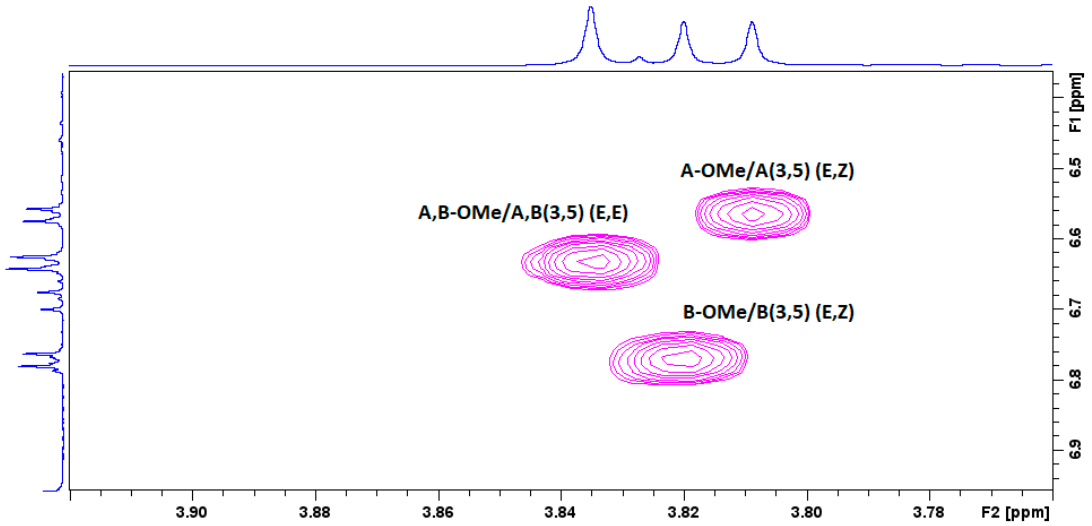

Figure S10: Part of ^{1}H-^{1}H-NOESY spectrum of 1 irradiated at λ=365 nm for 40 min, showing the methoxy-A,B(3,5) protons correlations for both isomers. See Scheme 1 for atom labeling.

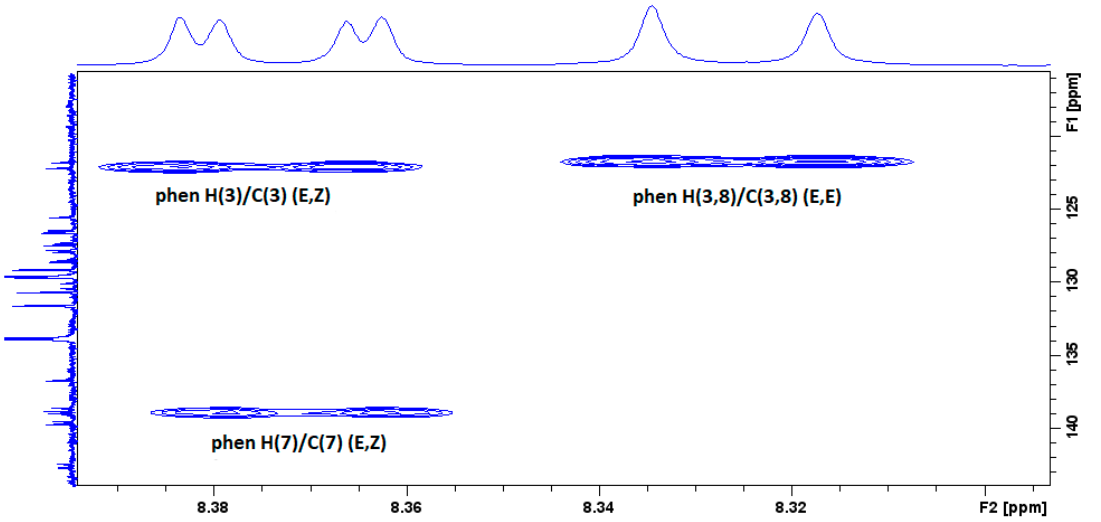

Figure S11: Part of ^{1}H-^{13}C-HSQC spectrum of 1 irradiated at λ=365 nm for 40 min, showing correlations of H(3)/C(3), H(7)/C(7) for E,Z isomer and H(3,8)/C(3,8) for E,E isomer. See Scheme 1 for atom labeling.

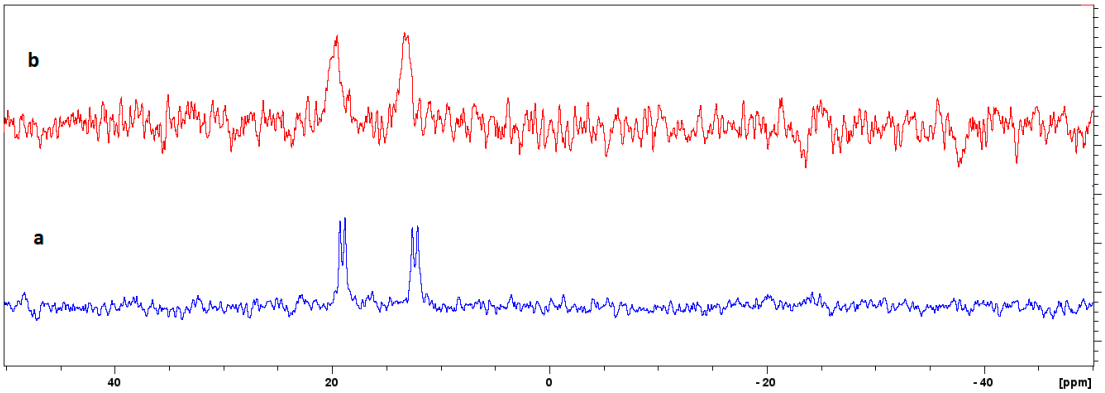

Figure S12: ^{31}P{^{1}H}-NMR spectra of $CDCl_3$ solutions of **1** (101.25 MHz, 298K): (a) using crystals of the compound; (b) irradiated at λ=365 nm for 40 min.

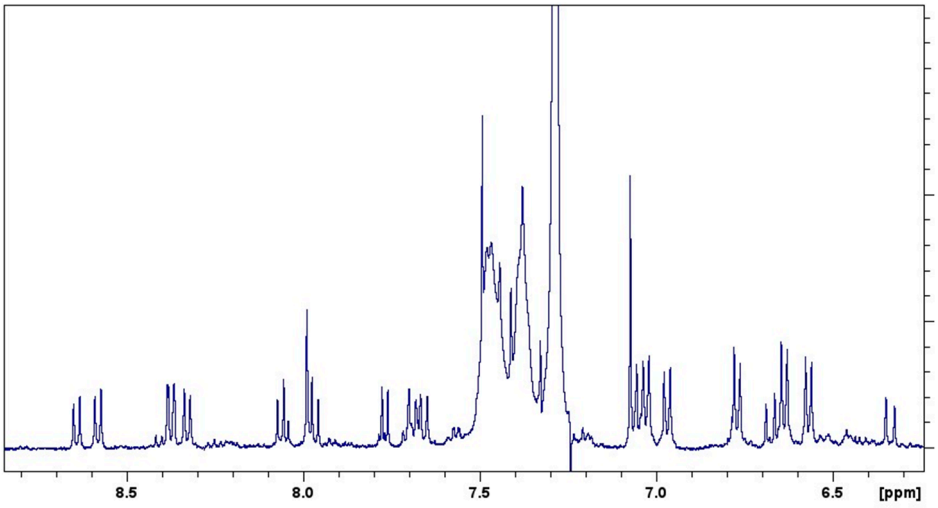

Figure S13: ^{1}H-NMR spectrum (aromatic region) of a $CDCl_3$ solution of compound **1** irradiated at λ=365 nm for an additional 2 hours (298K).

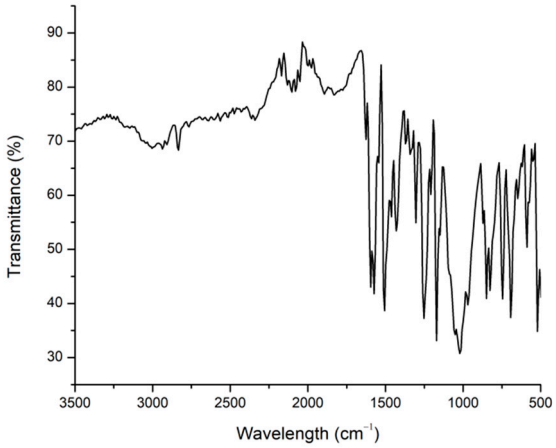

Figure S14: The ATR-IR spectrum of **1**.

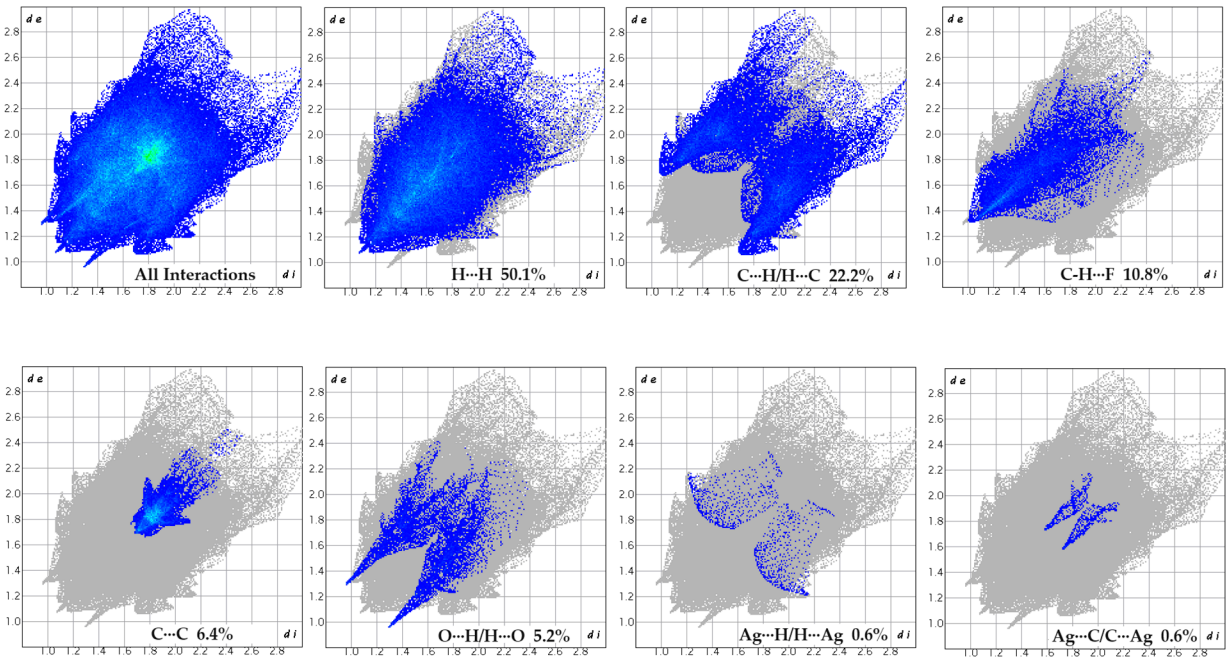

Figure S15: 2D fingerprint plots of $[AgL(PPh_3)]BF_4$.

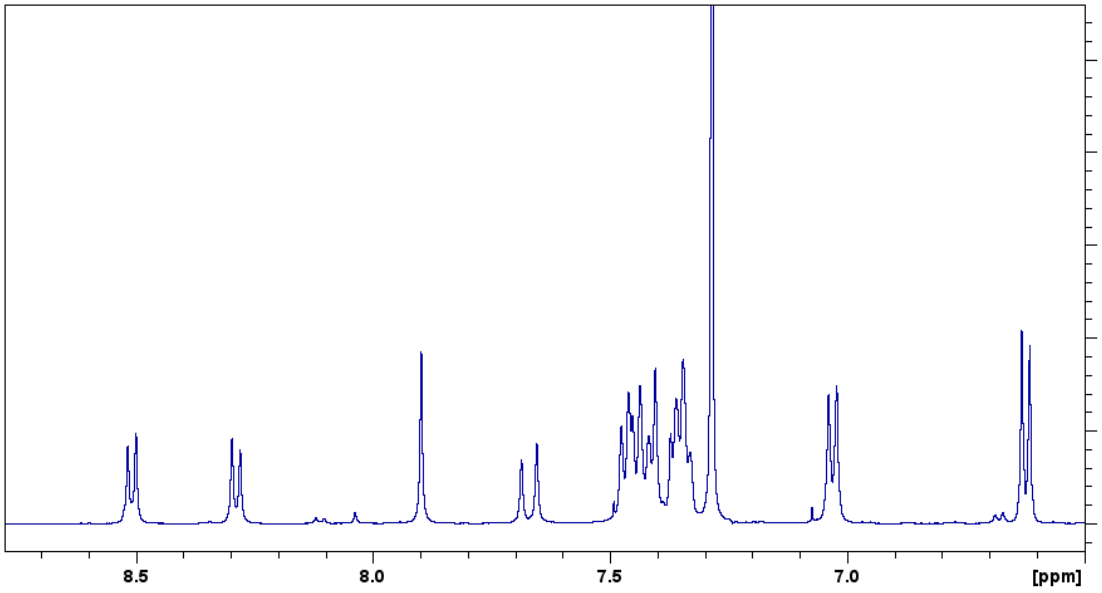

Figure S16: ^{1}H-NMR spectrum (aromatic region) of a $CDCl_3$ solution of **1** acquired immediately after recording the emission spectrum (298K).

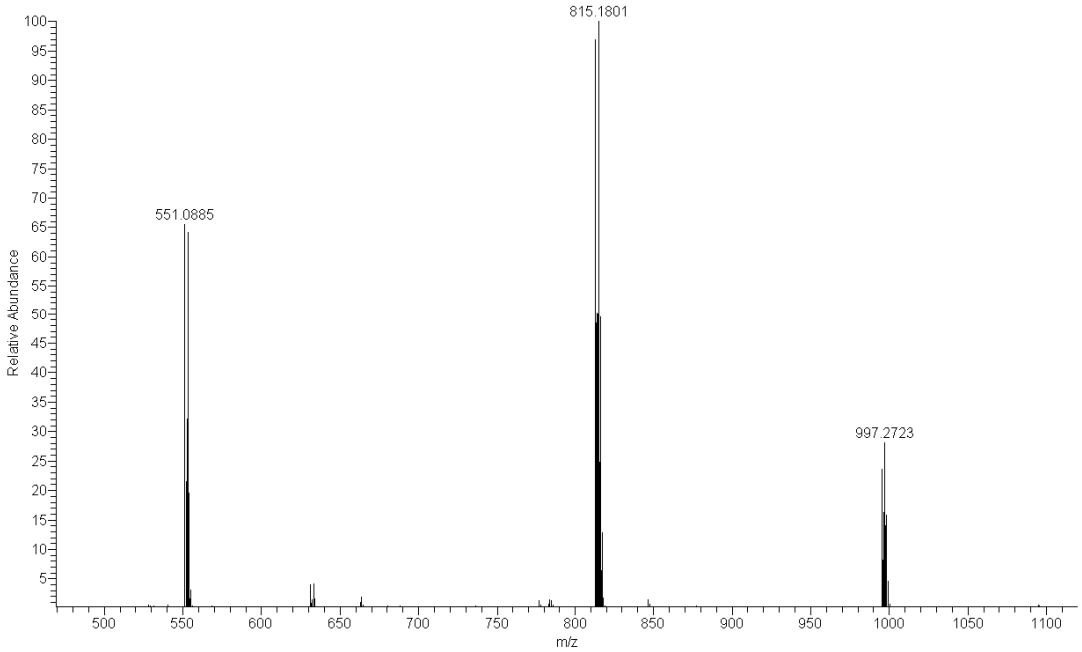

Figure S17: HR-ESI-MS spectrum of compound 1 in $CHCl_3$.

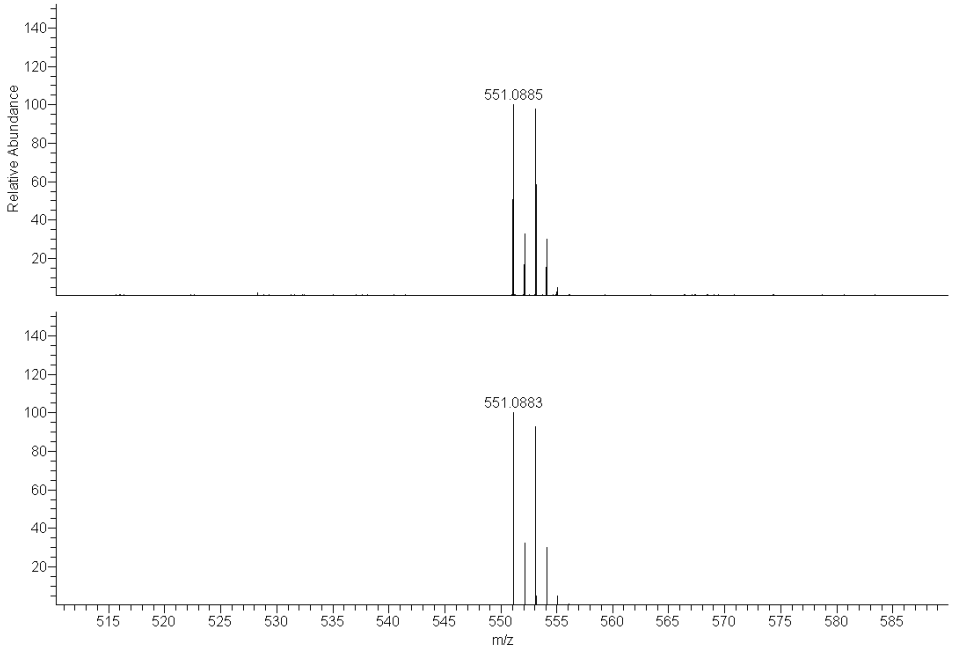

Figure S18: HR-ESI-MS spectrum of the fragment $[AgL]^+$ (top) and theoretical spectrum.

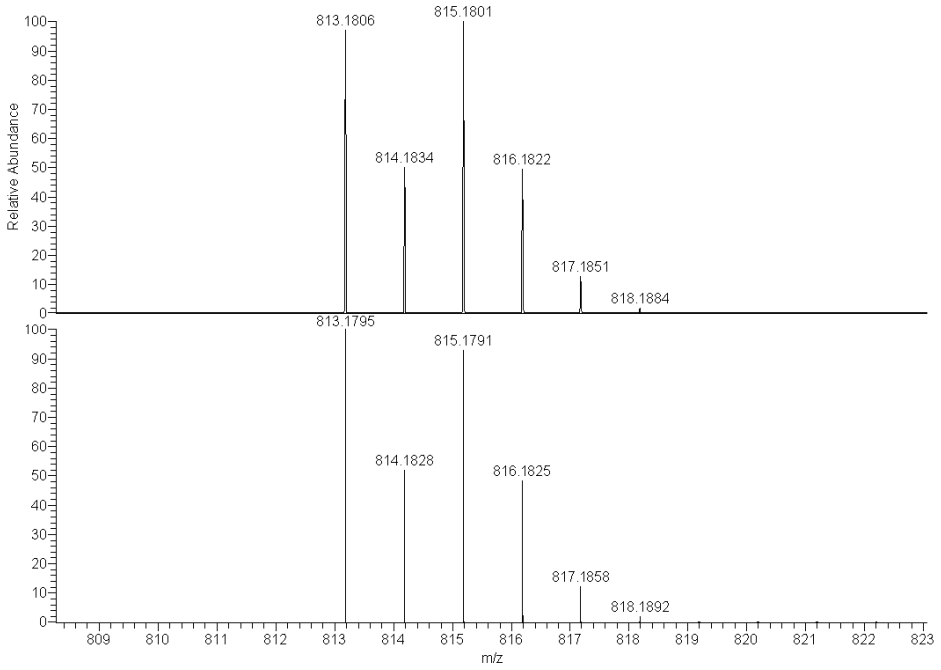

Figure S19: HR-ESI-MS spectrum of the fragment [AgL(PPh3)]+ (top) and theoretical spectrum.

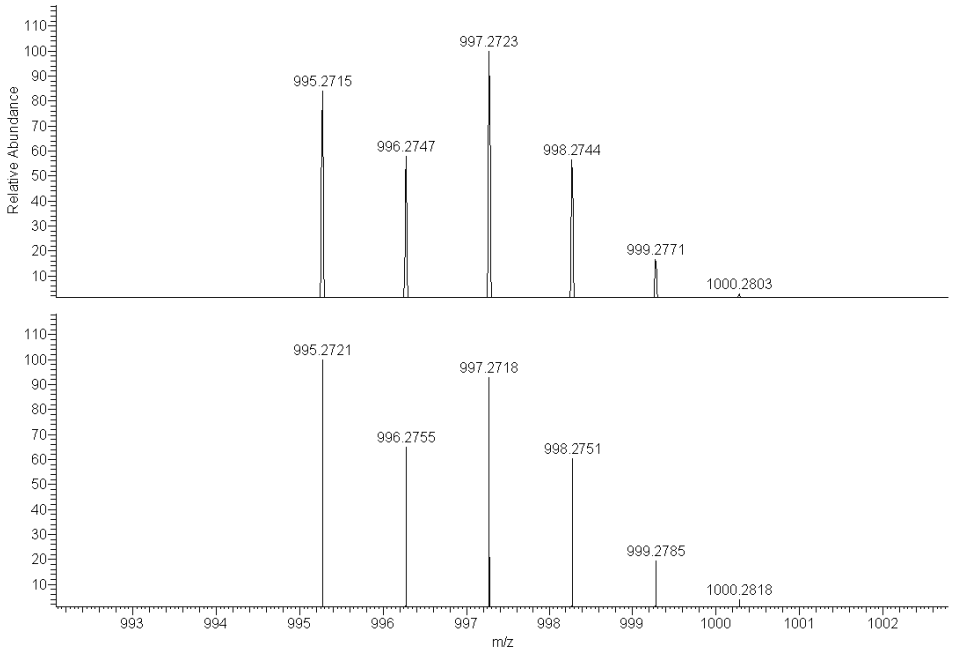

Figure S20: HR-ESI-MS spectrum of the fragment $[AgL_2]^+$ (top) and theoretical spectrum.

Table S1: ^{13}C-NMR data (δ,ppm) for L/PPh_3, and complex (E,E and E, Z isomers)

C Atoms	L(E,E)	Complex(E,E)	Δδ(E,E)*	C Atoms	Complex(E,Z)	Δδ(E,Z)*
C(3,8) phen	120.1	121.7	1.6	C(3) phen	122.1	2
C(4,7) phen	136.4	139.4	3	C(4) phen	139.6	3.2
C(5,6) phen	125.7	126.4	0.7	C(5) phen	127.3	1.6
C(2,9) phen	156.7	156.4	−0.3	C(6) phen	126.3	0.6
C(4a,4b) phen	127.8	126.5	−1.3	C(7) phen	138.9	2.5
C(10a,10b) phen	145.9	142.6	−3,3	C(8) phen	125.5	5.4
C(a,a′)	133.7	138.5	4.8	C(a) (E)	138.7	5
C(b,b′)	128	126.5	−1.5	C(b) (E)	126.4	−1.6
A,B C(2,6/2′,6′)	128.7	129	0.3	C(a′) (Z)	136.6	2.9
A,B C(3,5/3′,5′)	114.5	114.3	−0.2	C(b′) (Z)	127.7	−0.3
A,B C1	129.6	127.9	−1.7	A C(2,6)	129.1	0.4
A,B C4	160	160.7	−0.7	A C(3,5)	114.2	−0.3
A,B C(-OMe)	55.4	55.4	0	B C(2,6)	130.6	1.9
C_{ipso} PPh_3	-	130.4	-	B C(3,5)	114.3	−0.2
C_{ortho} PPh_3	-	133.8	-	A C(-OMe)	55.3	−0.1
C_{meta} PPh_3	-	129.5	-	B C(-OMe)	55.4	0
C_{para} PPh_3	-	131.5	-	C(2) phen	156.7	0
				C(9) phen	157	0.3
				C(4a) phen	128.5	0.7
				C(4b) phen	128.4	0.6
				C(10a) phen	142.6	−3.3
				C(10b) phen	142.3	−3.6
				A C(1)	127.8	−1.8
				A C(4)	160.7	0.7
				B C(1)	127.2	−2.4
				B C(4)	160.2	0.2
				C_{ipso} PPh_3	130.4	-
				C_{ortho} PPh_3	133.8	-
				C_{meta} PPh_3	129.5	-
				C_{para} PPh_3	131.5	-

*$\Delta\delta = \delta_{complex}$ (E,E or E,Z)-δ_{ligand} (ppm)

Table S2: Crystal data and structure refinement for C48 H39 Ag B F4 N2 O2 P at 296(2) K.

Empirical formula	C48 H39 Ag B F4 N2 O2 P
Formula weight	901.46
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.2795(3) Å, α = 98.070(2)° b = 11.8100(3) Å, β = 103.124(2)° c = 18.7503(4) Å, γ = 106.865(2)°
Volume	2068.90(10) $Å^3$
Z	2
Density (calculated)	1.447 g/cm^3
Absorption coefficient	0.586 mm^{-1}
F(000)	920
Crystal size	0.450 x 0.220 x 0.180 mm^3
θ range for data collection	2.502 to 24.997°
Index ranges	-12<=h<=12, -14<=k<=14, -22<=l<=22
Reflections collected	68781
Independent reflections	7274 [R_{int} = 0.0578]
Completeness to θ = 24.997°	99900%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7274 / 0 / 534
Goodness-of-fit	1.052
Final R indices [I > 2σ(I)]	R_{obs} = 0.0324, wR_{obs} = 0.0728
R indices [all data]	R_{all} = 0.0485, wR_{all} = 0.0790
Extinction coefficient	.
Largest diff. peak and hole	0.531 and -0.321 e·$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and $w=1/[\sigma^2(Fo^2)+(0.0314P)^2+1.4394P]$ where $P=(Fo^2+2Fc^2)/3$

Table S3: ^{1}H and ^{13}C NMR data (δ,ppm) for the ligand

H Atoms	δ (ppm)	C Atoms	δ (ppm)
H(3,8)	7.93	C(3,8)	120.1
H(4,7)	8.22	C(4,7)	136.4
H(5,6)	7.74	C(5,6)	125.7
-	-	C(2,9 phen)	156.7
-	-	C(4a,4b phen)	127.8
-	-	C(10a,10b phen)	145.9
H(a,a′)	7.77	C(a,a′)	133.7
H(b,b′)	7.62	C(b,b′)	128
A,B H(2,6/2′,6′)	7.68	A,B C(2,6/2′,6′)	128.7
A,B H(3,5/3′,5′)	6.99	A,B C(3,5/3′,5′)	114.5
-	-	A,B C(1)	129.6
-	-	A,B C(4)	160
A,B H(-OMe)	3.9	A,B C(-OMe)	55.4